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Improved Single-Site Chromium Catalysts with Electron Rich Indenyl Ligands for the Formation of Ultrahigh Molecular Weight Polyethylene

Helge-Boj Hansen,[a] Hubert Wadepohl,[a] and Markus Enders*[a]

Quinolyl functionalized indenyl chromium complexes with different substitution patterns were synthesized and evaluated as single site catalysts in ethylene polymerization. Adding substituents like a fused cyclohexyl ring or a $Si(CH_3)_3$ group to the indenyl moiety improve complex stability, solubility and catalytic activity compared to the unsubstituted analogues. Furthermore, the ability to incorporate 1-hexene into the polymer chain increased. Ultrahigh molecular weight polyethylene (UHMW-PE) or linear low density polyethylene (LLDPE) with very high molecular weight was obtained. Although other catalysts are able to incorporate more 1-hexene only a few systems are known, that combine substantial 1-hexene incorporation with very high activity and such high molecular weights. Consequently, these catalytic systems are attractive candidates in industrial processes for the production of improved polyethylene materials.

Introduction

Polyethylene (PE) of ultrahigh molecular weight (UHMW-PE) is a material with extraordinary properties like ultrahigh toughness and abrasion resistance. UHMW-PE fibers stronger than steel are commercially produced by an elaborate gel-spinning process.[1] However, very high melt viscosity due to massive chain entanglements of UHMW-PE make conventional melt processing procedures impossible and prevented large-scale use of UHMW-PE so far. Recent developments using a combination of molecular catalysts allowed the formation of disentangled nanophase separated UHMW-PE/PE blends which are processable by conventional techniques like injection molding, extrusion, and blow molding.[2] The key component for the production of the UHMW-PE fraction in such blends are organochromium complexes based on a donor-functionalized cyclopentadienyl (Cp) ligand[3] with derivative **1**[4] being the preferred pre-catalyst so far (Figure 1). After supporting the activated catalyst on silica gel ethylene is polymerized to UHMW-PE with high productivities. The catalytic activity depends on the substitution pattern at the five membered ring. Increasing the number of methyl groups leads to higher catalytic activities and a trimethylsilyl group is preferential too.[5] A fused thiophene at the Cp moiety increased activity and 1-hexene incorporation.[6] On the other hand, replacing the Cp ring by an indenyl ligand (see pre-catalyst **2**, Figure 1) leads to an increase in catalytic activity and to a higher ability for the incorporation of α-olefins as co-monomer.

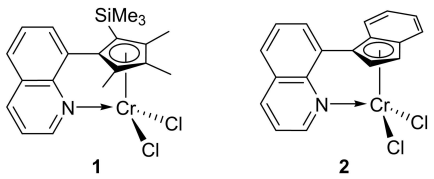

Figure 1. Literature known Cp and indenyl chromium pre-catalysts.[4,7]

The positive effects of alkyl substituents at the Cp ligand, which is accompanied by increased donor strength, could also play a role with related indenyl ligand systems. Many group IV complexes with highly substituted indenyl-moieties are known and polymerization behavior of these catalysts usually depends on substitution patterns.[8] A few derivatives of indenyl-chromium complexes with sterically demanding substituents and neutral pyridine donors are described in two patents.[9] The copolymerization behavior of chromium catalysts including an indenyl derivative was studied by Kaminsky et al.[10] and Romano et al. demonstrated that **2** allows the formation of disentangled UHMW-PE.[11] Our previous studies on quinolyl substituted Cp-chromium complexes focused on the substitution pattern at the Cp ring and its influence on ethylene 1-hexene copolymerization behavior respectively.[6] The indenyl chromium complex **2** which was investigated in earlier work has a low solubility combined with slow decomposition in solution as compared to similar Cp derivatives.[7,12] Adding substituents at the indenyl moiety could increase solubility and stability. The positive effects of substituents at the Cp-ring on polymerization behavior could improve the properties of the corresponding indenyl- chromium complexes. Such positive effects on polymerization behaviour can be attributed to the electron donating ability of the ligands and to an increase in

[a] H.-B. Hansen, Prof. Dr. H. Wadepohl, Prof. Dr. M. Enders
Anorganisch-Chemisches Institut, Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
E-mail: markus.enders@uni-heidelberg.de
https://www.uni-heidelberg.de/fakultaeten/chemgeo/aci/enders

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solubility.[13] The donor strength of substituted Cp ligands has frequently been evaluated by electrochemical, spectroscopic and theoretical methods.[14] A simple and powerful estimation of substituent effects relies on Hammett electronic parameters.[15] Therefore, we now report the synthesis of highly substituted indenyl quinolyl chromium complexes and their behavior regarding catalytic activity in ethylene polymerization and 1-hexene incorporation.

Results

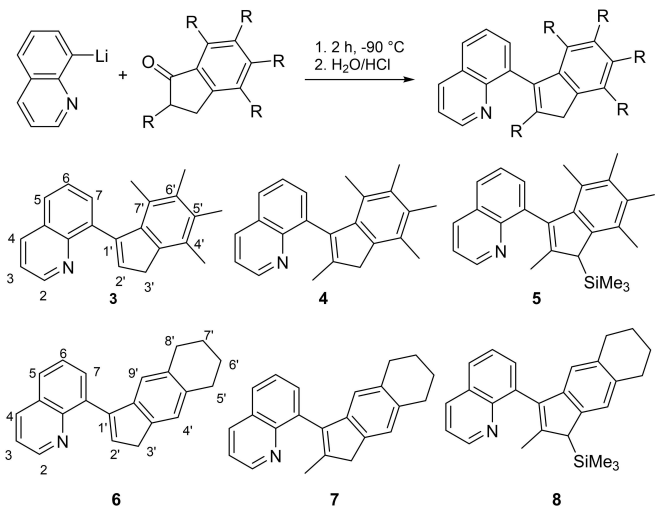
The highly substituted indenyl ligands (**3**–**8**, Scheme 1) have been synthesized via the reaction of 8-lithioquinoline with the corresponding indanone derivative. Indanones were synthesized according to literature procedures.[8a,c] We introduced four CH_3 groups at the aromatic backbone of the indene moiety in ligands **3**, **4** and **5** and gradually increased the level of substitution at the five membered ring by introducing a methyl group to position 2 in ligands **4** and **7** and an additional $SiMe_3$-group in ligands **5** and **8**. The lithium salts of **3**, **4**, **6**, **7** and **8** were obtained in situ by conversion of the corresponding ligand with *n*-butyllithium at low temperature in tetrahydrofuran and were used in the next step without further purification. For deprotonation of ligand **5** *n*-butyllithium proved to be insufficient. Due to steric hindrance between the $SiMe_3$-group and the neighbouring methyl-group at the benzene moiety, deprotonation is very slow and during longer reaction times the quinoline moiety was partially alkylated at the 2-position. To avoid alkylation, usually potassium hydride is used. However, with protio ligand **5** a secession of the $SiMe_3$-group occurred under formation of trimethylsilane. Therefore, the lithium salt of ligand **5** was prepared in situ by reaction with lithium diisopropylamide (LDA). The reaction was followed by NMR spectroscopy and was complete after 3 days at room temperature without observation of by-products.

Salt metathesis of the ligand lithium salts with $CrCl_3(THF)_3$ leads to the new complexes **9**–**14** (Figure 2). The solubility of the complexes differ significantly: **9** and **10** are almost insoluble in solvents like tetrahydrofuran or toluene, **11**, **12** and **13** are better soluble and **14** shows the highest solubility. Dichloromethane is able to dissolve all four complexes. One important point is the stability of the pre catalysts in solution as decomposition may lead to impure activated catalysts. Complex **2** slowly decomposes in solution over a couple of days. To a smaller extend, this was also observed for complexes **9** and **12**. However, all complexes which were substituted by a methyl group at the C_5 ring (**10**, **11**, **13** and **14**) showed practically no decomposition in solution during several days as monitored by NMR spectroscopy. ^{1}H NMR spectra of the paramagnetic complexes are in accordance with the results of previous NMR investigation of chromium complexes of that type.[4] Some ^{13}C NMR resonances of carbon atoms sufficiently distant from the paramagnetic chromium center could also be observed.

Crystals of **10**, **11**, **13** and **14** were obtained by slow diffusion of pentane into a solution of the corresponding complex in dichloromethane. The molecular structures were determined by single crystal X-ray diffraction and are similar to known related complexes[6,16] (Figure 3).

Ethylene homo and copolymerization

In order to get a first impression of the catalytic performance, all new complexes were tested in ethylene homopolymerization in solution after activation with MAO under equivalent conditions. The same solution experiment was conducted with the unsubstituted complex **2**. The most promising catalysts in terms of activity were then tested as catalyst in ethylene homopolymerization and ethylene /1-hexene copolymerization with silica



Scheme 1. General Synthesis of quinolyl functionalized indene protio-ligands and the new synthesized indenes.

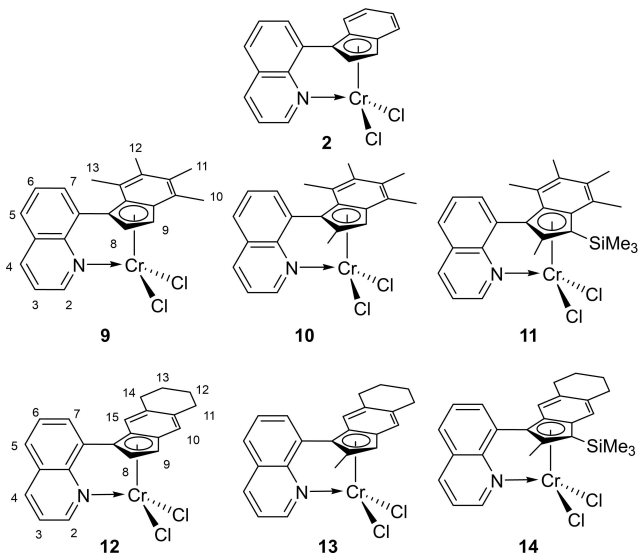


Figure 2. New complexes **9**–**14** and the formerly known indenyl-quinolyl complex **2**.

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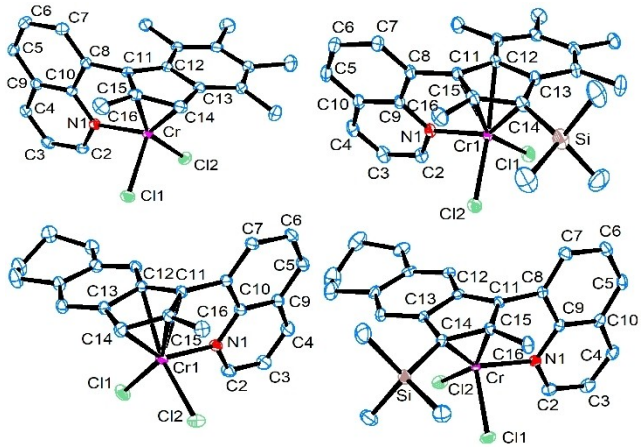

Figure 3. Molecular structures of **10** (top left), **11** (top right), **13** (bottom left, only one structure of two independent molecules is shown) and **14** (bottom right). Red: N, green: Cl, purple: Cr, beige: Si. H atoms are omitted for clarity, and displacement ellipsoids are drawn with 50% probability. For details of crystal structure analysis see SI. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of the complexes. Selected bond lengths (Å) and angles (deg.) (Cp means center of Cp ring, Cp-Cr-X means corresponding angle between atoms, Cp-Q means angle between planes): **10**: Cr-C11: 2.1867(15), Cr-C12: 2.2733(15), Cr-C13: 2.3148(15), Cr-C14: 2.2400(15), Cr-C15: 2.2409(15),Cr-N: 2.1095(13), Cr-Cl1: 2.2930(4), Cr-Cl2: 2.2766(4), Cp-Cr-Cl1: 124.00, Cp-Cr-Cl2: 125.21, Cp-Cr-N: 111.59, Cp-C11-C8: 170.37, Cp-Q: 82.71. **11**: Cr-C11: 2.182(2), Cr-C12: 2.243(2), Cr-C13: 2.297(2), Cr-C14: 2.252(2), Cr-C15: 2.245(2), 1.891, Cr-N: 2.113(2), Cr-Cl1: 2.2714(10), Cr-Cl2: 2.2915(9), Cp-Cr-Cl1: 123.74, Cp-Cr-Cl2: 125.06, Cp-Cr-N: 111.11, Cp-C11-C8: 169.84, Cp-Q: 76.30. **13** (values ins square brackets refer to the second independent molecule): Cr-C11: 2.1725(12) [2.1688(12)], Cr-C12: 2.2569(12) [2.2568(12)], Cr-C13: 2.3309(12) [2.3373(12)], Cr-C14: 2.2401(13) [2.2478(12)], Cr-C15: 2.2372(12) [2.2369(12)], Cr-N: 2.113(2) [2.0939(11)], Cr-Cl1: 2.2713(10) [2.2900(4)], Cr-Cl2: 2.2915(9) [2.2756(4)], Cp-Cr-Cl1: 125.58 [123.74], Cp-Cr-Cl2: 125.11 [125.06], Cp-Cr-N: 110.90 [111.16], Cp-C11-C8: 169.22 [169.71], Cp-Q: 75.87 [76.3]. **14**: Cr-C11: 2.192(3), Cr-C12: 2.274(3), Cr-C13: 2.299(3), Cr-C14: 2.249(3), Cr-C15: 2.217(3), Cr-N: 2.095(2), Cr-Cl1: 2.2868(8), Cr-Cl2: 2.2778(8), Cp-Cr-Cl1: 126.27, Cp-Cr-Cl2: 123.59, Cp-Cr-N: 111.82, Cp-C11-C8: 170.43, Cp-Q: 87.13.

as solid support. The results of polymerization experiments are shown in Tables 1–3.

A comparison of the results shows that all complexes with a higher level of substitution at the indene moiety have a higher catalytic activity than complex **2**. Homopolymerizations in solution were run over 15 to 30 minutes. Since the activity of the catalyst decrease with time, the averaged activities of 15 minute runs tend to be somewhat higher than those of 30 minute runs. The higher substituted complexes **9**, **11**, **12** and **14** show significantly higher activities than complex **2** in solution (Table 1). When these catalysts are supported on silica, activities tend to decrease slightly (Table 2, exp. 8–12). However, complexes **9** and **12** still show higher activities than complex **2**. Complexes **11** and **14**, where an additional methyl and a trimethylsilyl group is present, show the highest activity, about twice as high as the activity of complex **2** (Table 2, exp. 10, 12). It is known for this type of catalysts that they are able to produce PE in the UHMW-PE range when supported on SiO_2. This is attributed to a reduced reactivity of Al alkyl species for supported catalysts, so that chain transfer to Al alkyl species is suppressed..[6,17] For a comparison of molecular weights produced by catalysts with a different substitution pattern, we use data obtained from supported catalysts obtained from pre-catalyst **2** without substituents, from **9** and **11** (with tetramethylindenyl) and from **12** and **14** (cyclohexylindenyl). GPC and viscosity analysis show that molecular weights of PE produced by **9** (Mw = 476 000 g mol^{-1}) and **11** (Mw = 813 000 g mol^{-1}) is significantly lower than the PE produced by **2** (Mv = 1 888 000 g mol^{-1}), **12** (Mv = 1 510 000 g mol^{-1}) and **14** (Mw = 1 583 000 g mol^{-1}) (exp. 8, 11, 12). The GPC curves of two polymers produced by the less stable complexes **9** and **12** show broad molecular weight distributions resulting in large dispersities of $Đ = 9.5$ and 15.7, respectively. (see exp. 9 and 16). The maximum peak at high molecular weight and the large

Table 1. Ethylene polymerization with **2**/MAO and **9**–**14**/MAO catalytic systems.[a]

Exp.	Complex	Activity[b]	Mass [g] (time)	ΔH_m [J/g]	T_m [°C]	Cryst. [%]
1	**2**	3500	1.75 (15 min)	164	138.4	56.7
2	**9**	5800	2.90 (15 min)	177	137.2	61.3
3	**10**	3800	1.90 (15 min)	162	141.3	56.1
4	**11**	4200	2.10 (15 min)	211	135.5	73.1
5	**12**	4800	2.42 (15 min)	161	138.3	55.7
6	**13**	3900	1.95 (15 min)	173	141.1	59.8
7	**14**	4800	4.80 (30 min)	145	139.9	50.2

[a] Reaction conditions: 40 °C, 1 bar ethylene pressure, 100 mL toluene, 2 μmol [Cr], 2 mmol Al from MAO, [b] activity in g PE mmol^{-1} h^{-1} bar^{-1}.

Table 2. Ethylene polymerization with chromium complexes supported on SiO_2.[a]

Exp.	Complex	Activity[b]	Mass [g] (time)	IV[c] [dL/g]	Mw [g mol^{-1}]	Mn [g mol^{-1}]	Mv[d] [g mol^{-1}]	$Đ$	ΔH_m [J/g]	T_m [°C]	Cryst. [%]
8	**2**	2300	2.3 (30 min)	15.33	[e]	[e]	1 888 000	[e]	112	135.8	38.9
9	**9**	2900	2.9 (30 min)	[e]	476 000	50 000	[e]	9.5[f]	136	136.3	47.0
10	**11**	4800	4.8 (30 min)	[e]	813 000	124 000	[e]	6.6	134	134.8	46.5
11	**12**	2600	2.6 (30 min)	13.11	[e]	[e]	1 510 000	[e]	116	136.3	40.1
12	**14**	4700	4.7 (30 min)	[e]	1 583 000	324 000	[e]	4.9	134	135.3	46.6

[a] Reaction conditions: 40 °C, 1 bar ethylene pressure, 100 mL *n*-heptane, 1 mmol Triisobutylaluminum, 2 μmol [Cr], 2 mmol Al from MAO, [b] Activity in g PE mmol^{-1} h^{-1} bar^{-1}, [c] IV = intrinsic viscosity, [d] Mv calculated with Mark – Houwink equation from intrinsic viscosity with $K = 6.2 \cdot 10^{-4} dL \cdot g^{-1}$ α[19] = 0.7, [e] Not determined. [f] Bimodal distribution consisting of Mw = 853 834 g mol^{-1} ($Đ = 2.21$) and Mw = 117 095 g mol^{-1} ($Đ = 4.28$).

Table 3. Copolymerization of ethylene with 1-hexene using homogeneous and heterogeneous chromium catalytic systems.[a]

Exp.	Complex	1-hexene [ml]	Activity[b]	Mass [g] (time)	IV[c] [dL/g]	Mw [g mol^{-1}]	Mn [g mol^{-1}]	Mv[d] [g mol^{-1}]	$Đ$	CH_3/1000 C[e]	1-hexene[e] [wt %]	ΔH_m [J/g]	T_m[f] [°C]	Cryst.[g] [%]
13	**2**	2	3200	3.4 (30 min)	5.88	564 000	142 000	480 000	4.0	9.9	5.9	99.0	115	34.4
14	**9**	2	2900	2.9 (30 min)	5.88	553 000	181 000	480 000	3.1	9.9	5.9	89.0	116	30.8
15[h]	**11**	2	3300	3.3 (30 min)	b	397 000	119 000	[i]	3.3	10.0	6.0	88.9	118	30.7
16	**12**	2	3400	3.4 (30 min)	4.53	392 000	128 000	331 000	3.1	26.2	15.8	53.0	106	18.3
17[h]	**12**	2	2500	2.5 (30 min)	7.93	738 000	47 000	736 000	15.7[j]	17.1	10.3	75.0	113	26.4
18[h]	**14**	2	3700	3.7 (30 min)	b	679 000	119 000	[i]	5.7	16.3	9.8	76.4	111	26.4

[a] Reaction conditions: 40 °C, 1 bar ethylene pressure, 100 mL toluene, 2 μmol [Cr], 2 mmol Al from MAO, [b] Activity in g PE mmol^{-1} h^{-1} bar^{-1}, [c] IV = intrinsic viscosity, [d] Mv calculated with Mark–Houwink equation from intrinsic viscosity with $K = 6.2 \cdot 10^{-4} dL \cdot g^{-1}$ α[19] = 0.7, [e] Determined by ^{1}H-NMR, [f] Maximum of DSC curve, [g] Crystallinity calculated from theoretical melting enthalpy of 289 J g^{-1} for 100 % crystalline PE[20], [h] Supported catalyst, 100 mL *n*-heptane, 1 mmol Triisobutylaluminum, [i] Not measured, [j] Bimodal distribution consisting of Mw = 1 131 601 g mol^{-1} ($Đ$ = 2.9) and Mw = 126 129 g mol^{-1} ($Đ$ = 5.9).

shoulder at lower molecular weight can be separated into two overlapping peaks with $Đ$ = 2.9 and 5.9 (exp16), and $Đ$ = 2.5, 2.0 and 1.3 (exp 9) respectively (see Supporting Information for GPC traces). We attribute the broad molecular weight distributions to the low stability of the complexes in solution. Partial decomposition during the supporting procedure may lead to different active chromium centers causing the shoulder in GPC curves and the large $Đ$ values. The GPC traces of polymers produced by the other catalysts are approximately monomodal, however the dispersities are in the range from 3.1 to 6.6 and therefore above the theoretical value of 2.0 for ideal single-site catalysis. These deviations are due to tailings towards low molecular weight (see GPC in the Supporting Information). Such low molecular weight tailings affect the dispersity considerably if the molecular weight of the main peak is high. The sources of the low molecular weight fractions are unclear and might be due to some catalyst leaching or catalyst decompositions. The extreme moisture and oxygen sensitivity of the activated catalysts combined with very low catalyst concentrations makes it difficult to exclude such influences completely.

Complexes **9**, **11**, **12** and **14** were also tested in ethylene / 1-hexene copolymerization experiments. The comonomer incorporation strongly depends on the concentration of comonomer in the reaction vessel. To get an idea how good the activated complexes incorporate 1-hexene into the polymer chain, we used a small concentration of 1-hexene of approximately 0.16 mol l^{-1} (2 ml per 100 ml n-heptane) in every experiment. We did not observe an increase of catalytic activity when comonomer was present. This so called "comonomer effect" often occurs in copolymerization experiments.[18] Instead of that we noticed some decrease of activity of complexes **2**, **9** and **12**. (Table 3, exp. 13, 14, 16). However, the numbers from Table 1 are not fully comparable to the numbers of Table 2 and Table 3 as the polymerization times were different. On supported catalysts during 30 min polymerization pre-catalyst **12** gives almost the same catalytic activity with and without 1-hexene (entries 11 vs. 17), whereas **11** and **14** show a considerable decrease in catalytic activity in the presence of 1-hexene. The reason for this behavior remains unclear.

The amount of incorporated 1-hexene is represented by the number of CH_3 groups per 1000 carbon atoms in the polymer chain, which could be determined by ^{1}H-spectroscopy. Complex **2** and **9** showed an incorporation from up to 5.9 % (9.9 CH_3 /1000 C), whereas complex **12** incorporated 15.8 % (26.2 CH_3 /1000 C). This indicates that the substitution pattern at the indenyl moiety can influence the comonomer incorporation behavior significantly. When supported on silica, the activity and the amount of incorporated 1-hexene of complex **12** decreased. The GPC curve exhibits a shoulder at lower molecular weight resulting in a very high $Đ$ (exp. 17), similar to supported complex **9** (exp. 9). Complexes **9** and **12** are less stable in solution compared to the other complexes. Complexes **11** and **14**, tested on solid support, give the highest activity in copolymerization experiments. However, **11** showed an 1-hexene incorporation of 6 % and therefore the same behavior as **2** and its less substituted analogue **9** (exp. 15, 13, 14). Compared to that, complex **14** incorporated 9.8 % (16.3 CH_3 /1000 C) like the similar derivative **12** when supported on silica (exp. 17, 18). The copolymers that were produced in heterogeneous experiments have a significantly lower molecular weight than the homopolymers, but the molecular weight of the polymer produced by **14** (680 000 g mol^{-1}, 10 % 1-hexene, exp. 18) is again almost twice as high as that produced by **11** (390 000 g mol^{-1}, 6 % 1-hexene, exp. 15).

This leads to the conclusion that substitution by four methyl groups at the indenyl six membered ring does not seriously affect the comonomer incorporation compared to the unsubstituted complex **2** but leads to a lower molecular weight of the polymer. On the other hand, substitution with a fused cyclohexane increases comonomer incorporation. In addition to that the activity seems to correlate with the number of substituents at the five membered ring and the indenyl backbone as well, even though the effect of substitution at the Cp moiety is more noticeable. We attribute the increased

catalytic activity of the chromium center to the electron donating effects of alkyl and silyl substituents, which provide a more electron rich indenyl entity. We observed slow decomposition of complexes **9** and **12** in dichloromethane solution over several weeks, but we could not observe decomposition of complex **11** or **14** in solution at all. This indicates that steric effects caused by higher substitution at the five membered ring seem to enhance complex stability and can therefore increase catalytic activity.

Conclusion

We added several alkyl groups to donor functionalized indenyl ligands in order to enhance the electron donating properties of the ligands. Six new chromium (III) dichloro complexes were obtained and characterized by single crystal X-ray diffraction and by NMR spectroscopy. The complexes were used as catalysts in ethylene polymerization and ethylene/1-hexene copolymerization experiments after activation with MAO. The results of the experiments show that the catalytic activity increases with higher levels of substitution at the indenyl-moiety. The highly substituted complexes **11** and **14** showed the highest activities of 4800 and 4700 $kg\,mol^{-1}\,h^{-1}\,bar^{-1}$. Complex **14** where the indenyl is substituted by a fused cyclohexyl ring, a methyl and a $SiMe_3$ group, is able to produce UHMW-PE homopolymer with a molecular weight of 1 600 000 $g\,mol^{-1}$. Furthermore **14** allows the formation of a copolymer with a high 1-hexene content of up to 10% combined with a very high molecular weight in the range of 650 000 $g\,mol^{-1}$.

Experimental Section

General

All manipulations were carried out under argon or nitrogen atmosphere unless noted otherwise. Solvents like tetrahydrofuran (THF), ether, toluene and pentane were dried with an SPS-800 from mBRAUN and stored over molecular sieves. Dry *n*-heptane used for polymerization experiments was purchased from *Sigma Aldrich* and stored over molecular sieves prior to use. MAO was used as a 4.65 M solution in toluene (21–23% MAO, 7–9% aluminum alkyls). All other chemicals were purchased from chemical merchants (ABCR, Sigma Aldrich) and used without further purification. Deuterated solvents were purchased from Deutero GmbH or Sigma Aldrich and dried over K/Benzophenone (THF) or CaH_2 (dichloromethane) and distilled prior to use.

NMR spectra were recorded with a Bruker Avance III 600 or a Bruker Avance II 400 spectrometer. ^1H NMR spectra were referenced using the residual protio signal of the deuterated solvent. In ^{13}C NMR the resonances of the solvent were used. NMR spectra of polymers were recorded in d2-1,1,2,2-tetrachloroethane at temperatures between 60 °C–110 °C depending on the solubility. About 10 mg of the polymer was mixed with 0.5 mL of the solvent and heated for several hours until a clear solution was obtained. Elemental analyses were performed by the Mikroanalytisches Labor des Organisch-Chemischen Insituts der Universität Heidelberg on a Vario MICRO cube from Elementar. The melting points and enthalpies of the polymers were determined by differential scanning calorimetry with a DSC821e from Mettler Toledo. The samples were heated from 35 to 180 °C, cooled down to 35° and heated again to 180 °C. The heating and cooling rate was 10 °C/min respectively and the melting peaks and enthalpies were obtained by analyzing the second heating graph.

The determination of the molar mass distributions was carried out by high-temperature gel permeation chromatography in 1,2,4-trichlorobenzene at 150 °C using a PL-220 chromatograph (Polymer Laboratories) equipped with a differential refractive index (DRI) detector and a differential viscometer 210 R (Viscotek). The solvent was vacuum distilled under nitrogen and was stabilized with 0.2 wt% 2,6-di-tert-butyl-(4-methylphenol) (Aldrich) and was used at a flow rate of 1.0 $mL\,min^{-1}$. Columns were calibrated using 12 polyethylene samples with a narrow MWD defining universal calibration. The intrinsic viscosity of the polymers was measured with a PVS2 (Prozessor Viskositäts System) from LAUDA in decaline at 135 °C.

X-ray Structure Determination.

Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, sealed X-ray tube, graphite monochromator; complex 11) or an Agilent Technologies Supernova- E CCD diffractometer (Mo or Cu Kα radiation, microfocus X-ray tube, multilayer mirror optics; all other complexes). Data were corrected for air and detector absorption, Lorentz and polarization effects; absorption by the crystal was treated with a semiempirical multiscan method.[21] The structures were solved by the charge flip procedure[22] and refined by full-matrix least-squares methods based on F2 against all unique reflections.[23] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data, the positions of some hydrogen atoms were taken from difference Fourier syntheses and refined.

Catalytic Polymerization with Dissolved Catalyst

100 mL of toluene and 0.05 mL (0.2 mmol) of MAO solution is placed in a 250 mL spherical Schlenk flask equipped with magnetic stirrer and in the case of a copolymerization experiment, 2 mL of 1-hexene are added. The flask and the solution is saturated with ethylene and warmed to 40 °C with a water bath. 1 bar of Ethylene pressure is maintained during preparation and during polymerization. In a second flask, 2×10^{-6} mole of pre-catalyst **2**, **9**–**14** is dissolved/suspended in 2–4 ml of toluene and 0.39 mL (1.8 mmol) MAO solution is added. The activation process is accompanied by complete dissolution of suspended pre-catalyst and by a color change. After 5 min the activated catalyst solution is transferred to the 250 ml flask. Ethylene pressure is kept constant (1 bar) during the following 30 min. The polymerization is stopped by addition of 60 mL of a methanol / concentrated hydrochloric acid mixture (5:1). Then the mixture is stirred for 3 h at room temperature. The solid polymer is collected by filtration and washed with 300 mL of acetone. The solid is dispersed and stirred in a second portion of 300 mL of acetone for 18 h, before it is filtered and dried at 100 °C for 24 h.

Catalytic Polymerization with Supported Catalyst

The polymerization experiment with supported catalyst is performed in a spherical 250 mL Schlenk flask under ethylene atmosphere (1 atm) in 90 mL of n-heptane with 1 mL of 1 M

triisobutylaluminum solution in n-heptane at 40 °C for 30 min. For co-polymerizations, 2 mL of 1-hexene is added prior to catalyst addition.

Preparation of the Supported Catalyst

XPO-2326, a spray dried silica gel from Grace, is calcined at 600 °C for 6 h. A 2 μmol sample of the chromium complex is dissolved or suspended in 0.2 mL of toluene. Then 0.5 mL (2.3 mmol) of MAO solution is added, and the solution is stirred for 5 min before it is added dropwise within 1 min to the stirred 466 mg of calcined silica at −78 °C. The resulting solid is allowed to warm to room temperature and is stirred for 9 min. Then all volatiles are removed under reduced pressure before the supported catalyst is washed with 6 mL of n-heptane. It is then suspended in 10 ml of n-heptane and injected into the polymerization flask.

8-(4,5,6,7-tetramethyl-1H-inden-3-yl)quinoline (3)

A solution of 8-bromoquinoline (3.50 g, 16.8 mmol, 1.00 eq) in THF (30 ml) was cooled to −90 °C before a 1.4 M solution of *sec*-BuLi (12.0 ml, 16.8 mmol, 1.00 eq) in cyclohexane was added dropwise over 20 min. After stirring for 10 min at −90 °C, a solution of 4,5,6,7-tetramethyl-1H-indan-1-one (3.17 g, 16.8 mmol, 1.00 eq) in THF (16 ml) was added over 5 min at −90 °C. After the cooling bath was removed the mixture was left to stir for 2 h at room temperature. Then the reaction mixture was quenched and acidified with conc. HCl (15 ml) and stirred for 30 min at room temperature. The mixture was treated with aqueous ammonia until it became basic, the layers were separated, and the aqueous layer was extracted with dichloromethane (3×50 ml). The solvent and volatile impurities were removed at 150 °C and a pressure of 3×10^{-2} mbar. The residue was purified by column-chromatography (stationary phase: silica gel; mobile phase: petrol ether : ethyl acetate : triethylamine ether = 20:1:0.5, R_f:0.36) to give a yellow solid (865 mg, 2.89 mmol, 17 %) that was stored at −38 °C.

^{1}H-NMR (600 MHz, C_6D_6): δ = 1.79 (s, 3H, C$\underline{H}_3$), 2.03 (s, 3H, C$\underline{H}_3$), 2.17 (s, 3H, C$\underline{H}_3$), 2.19 (s, 3H, C$\underline{H}_3$), 3.22 (dd, *J* = 22.8, 1,8 Hz, 1H, C$\underline{H}_2^{3'}$), 3.28 (dd, *J* = 22.8, 1.8 Hz, 1H, C$\underline{H}_2^{3'}$), 6.38 (t, *J* = 2.0 Hz, 1H, $H^{2'}$), '), 6.74 (dd, *J* = 8.2, 4.0 Hz, 1H, H^3), 7.26 (dd, *J* = 8.2, 6.9 Hz, 1H, H^6), 7.44 (dd, *J* = 8.2, 1.4 Hz, 1H, H^7), 7.57 (dd, *J* = 8.3, 1.7 Hz, 1H, H^4), 7.67 (dd, *J* = 7.0, 1.4 Hz, 1H, H^5), 8.62 (dd, *J* = 4.0, 1.9 Hz, 1H, H^2). **^{13}C-NMR** (150 MHz, C_6D_6): δ = 15.86 (C$\underline{H}_3$), 16.20 (C$\underline{H}_3$), 16.27 (C$\underline{H}_3$), 16.46 (C$\underline{H}_3$), 37.86 ($C^{3'}$), 121.12 (C^3), 126.45 (C^6), 127.50 (C^7), 127.69 (C_q), 128.46 (C_q), 128.57 (C_q), 129.65 (C^5), 131.34 (C_q), 132.15 ($C^{2'}$)133.49 (C_q), 135.61 (C^4), 141.03 (C_q), 141.45 (C_q), 142.37 (C_q), 146.83 (C_q), 148.53 (C_q), 150.10 (C^2).

8-(2,4,5,6,7-pentamethyl-1H-inden-3-yl)quinoline (4)

A solution of 8-bromoquinoline (4.63 g, 22.2 mmol, 1.00 eq) in THF (40 ml) was cooled to −90 °C before a 1.4 M solution of *sec*-BuLi (15.9 ml, 22.2 mmol, 1.00 eq) in cyclohexane was added dropwise over 20 min. After the mixture stirred for 10 min at −90 °C, a solution of 2,4,5,6,7-pentamethyl-1H-indan-1-one (4.50 g, 22.2 mmol, 1.00 eq) in THF (18 ml) was added over 5 min at −90 °C. After the cooling bath was removed the mixture was left to stir for 2 h at rt. Then the reaction mixture was quenched and acidified with conc. HCl (15 ml) and stirred for 30 min at rt. After the mixture was made basic with aqueous ammonia, the layers were separated, and the aqueous layer was extracted with dichloromethane (3× 50 ml). The solvent and volatile impurities were removed at 175 °C and a pressure of 2×10^{-1} mbar. The residue was purified by column-chromatography (silica, petrol ether : ethyl acetate : triethylamine ether = 15:1:0.5, R_f: 0.22) to give a yellow solid (2.60 g, 8.31 mmol, 37 %) that was stored at −38 °C.

^{1}H-NMR (600 MHz, C_6D_6): δ = 1.72 (s, 3H, C$\underline{H}_3$), 1.85 (s, 3H, C$\underline{H}_3$), 2.02 (s, 3H, C$\underline{H}_3$), 2.20 (s, 3H, C$\underline{H}_3$), 2.22 (s, 3H, C$\underline{H}_3$), 3.18 (s, 2H, C$\underline{H}_2^{3'}$), 6.76 (dd, *J* = 8.2, 4.0 Hz, 1H, H^3), 7.30 (dd, *J* = 8.2, 6.9 Hz, 1H, H^6), 7.46 (dd, *J* = 8.2, 1.5 Hz, 1H, H^7), 7.55 (dd, *J* = 6.9, 1.5 Hz, 1H, H^4), 7.61 (dd, *J* = 6.9, 1.5 Hz, 1H, H^5), 8.65 (dd, *J* = 4.0, 1.8 Hz, 1H, H^2). **^{13}C-NMR** (150 MHz, C_6D_6): δ = 15.07 (C$\underline{H}_3$), 15.70 (C$\underline{H}_3$), 16.23 (C$\underline{H}_3$), 16.26 (C$\underline{H}_3$), 16.54 (C$\underline{H}_3$), 42.62 ($C^{3'}$), 121.13 (C^3), 126.47 (C^6), 127.34 (C^7), 128.10 (C_q), 128.35 (C_q), 128.74 (C_q), 130.20 (C_q), 130.63 (C^4), 133.44 (C_q), 135.76 (C^5), 139.39 (C_q), 139.85 (C_q), 139.96 (C_q), 140.58 (C_q), 143.52 (C_q), 148.57 (C_q), 150.21 (C^2).

8-(2,4,5,6,7-pentamethyl-1-(trimethylsilyl)-1H-inden-3-yl) quinoline (5)

A solution of Compound **18** (1.5 g, 4.79 mmol, 1.00 eq) in THF (25 ml) was added to a suspension of pure potassium hydride (192 mg, 4.79 mmol, 1.00 eq) in THF (15 ml) under an argon atmosphere in a glovebox. The resulting deep blue mixture was stirred for 18 h at rt before chlorotrimethylsilane (0.61 ml, 4.83 mmol, 1.01 eq) was added and stirred for another 24 h. The solvent was removed under reduced pressure and the residue was purified by column-chromatography (silica, petrol ether : ethyl acetate : triethylamine ether = 15:1:1, R_f: 0.36) to yield the target compound **5** (1.38 g, 3.57 mmol, 75 %) as a light-yellow solid.

^{1}H-NMR (600 MHz, C_6D_6): δ = 0.04 (s, 9H, SiC$\underline{H}_3$), 1.76 (s, 3H, C$\underline{H}_3$), 1.90 (s, 3H, C$\underline{H}_3$), 2.02 (s, 3H, C$\underline{H}_3$), 2.20 (s, 3H, C$\underline{H}_3$), 2.25 (s, 3H, C$\underline{H}_3$), 3.51 (s, 1H, $H^{3'}$), 6.73 (dd, *J* = 8.2, 4.1 Hz, 1H, H^3), 7.35 (dd, *J* = 8.2, 6.9 Hz, 1H, H^6), 7.50 (dd, *J* = 8.2, 1.4 Hz, 1H, H^7), 7.61 (dd, *J* = 8.2, 1.8 Hz, 1H, H^4), 7.71 (dd, *J* = 6.9, 1.4 Hz, 1H, H^5), 8.56 (dd, *J* = 4.0, 1.8 Hz, 1H, H^2). **^{13}C-NMR** (150 MHz, C_6D_6): δ = −0.69 (Si$\underline{C}H_3$), 15.93 (C$\underline{H}_3$), 16.20 (C$\underline{H}_3$), 16.37 (C$\underline{H}_3$), 16.42 (C$\underline{H}_3$), 19.31 (C$\underline{H}_3$), 48.99 ($C^{3'}$), 121.09 (C^3), 126.31 (C_q), 126.45 (C^6), 126.88 (C_q), 127.30 (C^7), 128.80 (C_q), 129.84 (C_q), 130.75 (C^5), 132.01 (C_q), 135.71 (C^4),137.60 (C_q), 141.13 (C_q), 142.16 (C_q), 142.40 (C_q), 142.72 (C_q), 148.70 (C_q), 150.19 (C^2).

8-(5,6,7,8-tetrahydro-1H-cyclopenta[b]naphthalen-3-yl) quinoline (6)

A solution of 8-bromoquinoline (3.10 g, 14.9 mmol, 1.00 eq) in THF (25 ml) was cooled to −90 °C before a 1.4 M solution of *sec*-BuLi (10.64 ml, 14.9 mmol, 1.00 eq) in cyclohexane was added dropwise over 15 min. After the mixture stirred for 10 min at −90 °C, a solution of 2,3,5,6,7,8-hexahydro-1H-cyclopenta[b]naphthalen-1-one (2.78 g, 14.9 mmol, 1.00 eq) (X) in THF (16 ml) was added over 5 min at −90 °C. After the cooling was removed the mixture was left to stir at rt for 16 h. Then the reaction mixture was quenched and acidified with conc. HCl (15 ml) and stirred for 30 min at rt. After the mixture was made basic with aqueous ammonia, the layers were separated', and the aqueous layer was extracted with dichloromethane (3×50 ml). The solvent and volatile impurities were removed at 200 °C and a pressure of 2×10^{-1} mbar. The residue was purified by column-chromatography (silica, petrol ether: ethyl acetate: triethylamine = 20:1:1, R_f: 0.27) to give a yellow solid (1.22 g, 4.11 mmol, 28 %) that was stored at −38 °C.

^{1}H-NMR (600 MHz, C_6D_6): δ = 1.62 (m, 4H, C$\underline{H}_2^{6'}$, C$\underline{H}_2^{7'}$), 2.58 (t, *J* = 6.12 Hz, 2H, C$\underline{H}_2^{5'}$), 2.75 (t, *J* = 6.23 Hz, 2H, C$\underline{H}_2^{8'}$), 3.41 (m, 2H, C$\underline{H}_2^{3'}$), 6.72 (t, *J* = 2.0 Hz, 1H, $H^{2'}$), 6.77 (dd, *J* = 8.2, 4.0 Hz, 1H, H^3), 7.10 (s, 1H, $H^{9'}$), 7.11 (s, 1H, $H^{4'}$), 7.28 (dd, *J* = 7.9, 7.2 Hz, 1H, H^6), 7.42 (dd, *J* = 8.1, 1.3 Hz, 1H, H^7), 7.59 (dd, *J* = 8.2, 1.7 Hz, 1H, H^4), 7.81 (dd, *J* = 7.1, 1.4 Hz, 1H, H^5), 8.71 (dd, *J* = 3.9, 1.8 Hz, 1H, H^2). **^{13}C-NMR** (150 MHz, C_6D_6): δ = 23.94 ($C^{7'}$), 24.00 ($C^{6'}$), 30.12 ($C^{5'}$), 30.13 ($C^{8'}$),

38.41 ($C^{3'}$), 121.22 (C^{3}), 121.96 ($C^{9'}$), 124.79 ($C^{4'}$), 126.45 (C^{6}), 127.70 (C^{7}), 128.93 (C_q), 129.95 (C^{5}), 133.22 ($C^{2'}$), 133.43 (C_q), 134.60 (C_q), 135.78 (C^{4}), 137.37 (C_q), 141.78 (C_q), 143.96 (C_q), 144.53 (C_q), 147.64 (C_q), 150.03 (C^{2}).

8-(2-methyl-5,6,7,8-tetrahydro-1H-cyclopenta[b] naphthalen-3-yl)quinoline (7)

A solution of 8-bromoquinoline (2.40 g, 11.5 mmol, 1.00 eq) in THF (20 ml) was cooled to −90 °C before a 1.4 M solution of *sec*-BuLi (8.24 ml, 11.5 mmol, 1.00 eq) in cyclohexane was added dropwise over 20 min. After the mixture stirred for 10 min at −90 °C, a solution of 2-methyl-2,3,5,6,7,8-hexahydro-1H-cyclopenta[b] naphthalen-1-one (2.31 g, 11.5 mmol, 1.00 eq) in THF (10 ml) was added over 5 min at −90 °C. After the cooling was removed the mixture was left to stir for 2 h at rt. Then the reaction mixture was quenched and acidified with conc. HCl (18 ml). Ethanol (6 ml) was added to mix the aqueous and the organic layer and the resulting solution was stirred for 15 min at rt. After the mixture was made basic with aqueous ammonia dichloromethane (50 ml) were added. The layers were separated, and the aqueous layer was extracted with dichloromethane (3×50 ml). The solvent and volatile impurities were removed at 175 °C and a pressure of 2×10^{-1} mbar. The residue was purified by column-chromatography (silica, petrol ether : ethyl acetate : triethylamine ether = 20 : 1.5 : 1, R_f: 0.32) to give the target compound **7** as a yellow solid (1.85 g, 5.95 mmol, 52 %) that was stored at −38 °C.

^{1}H-NMR (600 MHz, C_6D_6): δ = 1.55-1.67 (m, 4H, $CH_2^{6'}$,$CH_2^{7'}$), 1.95 (s, 3H, CH_3), 2.48–2.58 (m, 2H, CH_2), 2.77 (m, 2H, CH_2), 3.28-3.42 (m, 2H, $CH_2^{3'}$), 6.76 (dd, *J* = 8.2, 4.0 Hz, 1H, H^3), 6.83 (s, 1H, $H^{9'}$), 7.10 (s, 1H, $H^{4'}$), 7.32 (dd, *J* = 8.0, 7.0 Hz, 1H, H^6), 7.47 (dd, *J* = 8.2, 1.4 Hz, 1H, H^7), 7.61 (dd, *J* = 8.2, 1.8 Hz, 1H, H^4), 7.68 (dd, *J* = 7.0, 1.4 Hz, 1H, H^5), 8.69 (dd, *J* = 4.0, 1.8 Hz, 1H, H^2). **^{13}C-NMR** (150 MHz, C_6D_6): δ = 15.52 (CH_3), 23.97 ($C^{7'}$), 24.07 ($C^{6'}$), 30.06 ($C^{5'}$), 30.14 ($C^{8'}$), 42.93 ($C^{3'}$), 120.67 ($C^{9'}$), 121.19 (C^3), 124.31 ($C^{4'}$), 126.49 (C^6), 127.61 (C^7), 129.03 (C_q), 130.91 (C^5), 132.47 (C_q), 134.63 (C_q), 135.87 (C^4), 136.98 (C_q), 137.96 (C_q), 140.23 (C_q), 141.23 (C_q), 146.46 (C_q), 147.78 (C_q), 150.12 (C^2).

8-(2-methyl-1-(trimethylsilyl)-5,6,7,8-tetrahydro-1H-cyclopenta[b]naphthalen-3-yl)quinoline (8)

Synthetic procedure similar to the synthesis of **5**. Scale: Compound **7** (0.9 g, 2.89 mmol, 1.00 eq), potassium hydride (116 mg, 2.89 mmol, 1.00 eq), $SiMe_3Cl$ (0.4 ml, 3.18 mmol, 1.10 eq), purification (silica, PE:EE:TEA = 25 : 1 : 1, R_f: 0.45), yield: 74 %

^{1}H-NMR (600 MHz, C_6D_6): Isomer 1: δ = 0.28 (s, 9H, $SiCH_3$), 1.62-1.71 (m, 4H, $CH_2^{6'}$, $CH_2^{7'}$), 2.04 (s, 3H, CH_3), 2.49-2.67 (m, 4H, $CH_2^{5'}$, $CH_2^{8'}$), 3.45 (s, 1H, $H^{3'}$), 6.77 (dd, *J* = 8.2, 4.0 Hz, 1H, H^3), 6.99 (s, 1H, $H^{9'}$), 7.30 (s, 1H, $H^{4'}$), 7.32 (dd, *J* = 7.9, 7.2 Hz, 1H, H^6), 7.46 (dd, *J* = 8.1, 1.3 Hz, 1H, H^7), 7.61 (dd, *J* = 8.2, 1.8 Hz, 1H, H^4), 7.77 (dd, *J* = 7.0, 1.4 Hz, 1H, H^5), 8.68 (dd, *J* = 4.0, 1.8 Hz, 1H, H^2). Isomer 2: δ = 0.06 (s, 9H, $SiCH_3$), 1–54-1.61 (m, 4H, $CH_2^{6'}$, $CH_2^{7'}$), 2.05 (s, 3H, CH_3), 2.80-2.92 (m, 4H, $CH_2^{5'}$, $CH_2^{8'}$), 3.42 (s, 1H, $H^{3'}$), 6.76 (dd, *J* = 8.2, 4.0 Hz, 1H, H^3), 6.89 (s, 1H, $H^{9'}$), 7.22 (s, 1H, $H^{4'}$), 7.37 (dd, *J* = 8.1, 7.1 Hz, 1H, H^6), 7.51 (dd, *J* = 8.2, 1.4 Hz, 1H, H^7), 7.63 (dd, *J* = 8.2, 1.8 Hz, 1H, H^4), 7.72 (dd, *J* = 6.8, 1.5 Hz, 1H, H^5), 8.68 (dd, *J* = 4.0, 1.8 Hz, 1H, H^2).

^{13}C-NMR (150 MHz, C_6D_6): Isomer 1: δ = −1.49 ($SiCH_3$), 16.92 (CH_3), 24.07 ($C^{7'}$), 24.19 ($C^{6'}$), 30.11 ($C^{5'}$), 30.41 ($C^{8'}$), 49.45 ($C^{3'}$), 120.21 ($C^{9'}$), 120.99 (C^3), 123.69 ($C^{4'}$), 126.45 (C^6), 127.29 (C^7), 129.04 (C_q), 131.06 (C^5), 131.48 (C_q), 133.63 (C_q), 135.21 (C_q), 135.86 (C^4), 137.37 (C_q), 142.60 (C_q), 143.98 (C_q), 145.44 (C_q), 147.75 (C_q), 149.96 (C^2). Isomer 2: δ = −1.77 ($SiCH_3$), 16.40 (CH_3), 24.02 ($C^{7'}$), 24.15 ($C^{6'}$), 30.05 ($C^{5'}$), 30.42 ($C^{8'}$), 48.68 ($C^{3'}$), 120.60 ($C^{9'}$), 121.17 (C^3), 123.73 ($C^{4'}$), 126.53 (C^6), 127.53 (C^7), 129.08 (C_q), 131.30 (C^5), 131.53 (C_q), 133.56 (C_q), 135.87 (C^4), 136.67 (C_q), 137.73 (C_q), 141.98 (C_q), 142.70 (C_q), 145.56 (C_q), 147.92 (C_q), 150.16 (C^2).

Complex 9

A solution of **3** (300 mg, 1.00 mmol, 1.00 eq) in THF (10 ml) was cooled to −90 °C before a 1.6 M solution of *n*-BuLi (631 µl, 1.01 mmol, 1.00 eq) was added dropwise over 15 min. The reaction mixture turned deep blue rapidly and was stirred for another 15 min at −90 °C. After warming to room temperature this solution was added via a cannula to a suspension of $CrCl_3(THF)_3$ (375 mg, 1.00 mmol, 1.00 eq) in THF (15 ml) and was stirred for 20 h to form a dark solution with a precipitate. The powdery precipitate was separated from the solution with a centrifuge and was washed with THF (3×2 ml) and pentane (2×10 ml) and dried under vacuum to yield the target complex **9** (198 mg, 471 µmol, 47 %) as a dark green solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ = −48.85 (H^4), −36.50 (CH_3^{11}), −12.14 (H^5), −7.56 (CH_3^{13}), 6.79 (H^7), 11.04 (H^6), 32.19 (CH_3^{12}), 46.08 (CH_3^{10}), 50.22 (H^3). **EI-MS** (m/z): 420.04 [34 %], 298.16 [38 %], 384.06 [100 %]. **Elemental Analysis** calc. (found) for $C_{22}H_{20}Cl_2CrN$: C: 62.72 (62.88); H: 5.79 (5.61); N: 3.32 (3.16)

Complex 10

A solution of **4** (300 mg, 957 µmol, 1.00 eq) in THF (10 ml) was cooled to −90 °C before a 1.6 M solution of *n*-BuLi (598 µl, 957 µmol, 1.00 eq) was added dropwise over 15 min. The reaction mixture turned deep blue rapidly and was stirred for another 15 min at −90 °C. After warming up to rt this solution was added via cannula to a suspension of $CrCl_3(THF)_3$ (359 mg, 957 mmol, 1.00 eq) in THF (12 ml) and was stirred for 16 h to form a dark solution with a precipitate. The powdery precipitate was separated from the solution with a centrifuge and washed with THF (3×2 ml) and pentane (2×10 ml) and dried under vacuum to yield the target complex **10** (141 mg, 324 µmol, 34 %) as a dark green solid.

^{1}H-NMR (600 MHz, CD_2Cl_2): δ = −48.81 (H^4), −38.24 (CH_3^{11}), −11.33 (H^5), −7.98 (CH_3^{13}), 6.85 (H^7), 10.84 (H^6), 33.80 (CH_3^{12}), 45.82 (CH_3^{10}), 49.32 (CH_3^{8}), 50.74 (H^3). **^{13}C-NMR** (150 MHz, CD_2Cl_2,): δ = −34.94, 35.49, 71.55, 114.03, 168.59. **EI-MS** (m/z [rel. int.]): 398.08 (100 %), 362.10 (44 %), 282.13 (36 %), 434.05 (30 %). **Elemental Analysis** calc. (found) for $C_{23}H_{22}Cl_2CrN$: C: 63.46 (62.96); H: 5.09 (5.24); N: 3.22 (2.78).

Complex 11

A solution of **5** (300 mg, 778 µmol, 0.98 eq) in THF (4 ml) was cooled to −78 °C before a freshly prepared 0.46 M solution of lithium diisopropylamide (LDA) (1.73 ml, 794 µmol, 1.00 eq) was added dropwise over 15 min. After warming up to rt this solution was stirred for 2 d and then added via cannula to a suspension of $CrCl_3(thf)_3$ (292 mg, 778 mmol, 0.98 eq) in THF (10 ml). The mixture was stirred for 16 h to form a dark green solution. The solvent was removed under reduced pressure and toluene (20 ml) was added. The resulting suspension was stirred for 2 h, the toluene was removed in vacuum and the residue was extracted with a mixture of dichloromethane and pentane (1 : 2; 9 ml). This solution was dried under vacuum and the residue was crystallized by diffusion of pentane into a solution of dichloromethane. After the solid was washed with pentane (2×10 ml) complex **11** (185 mg, 365 µmol, 46 %) was obtained as dark green crystals. **^{1}H-NMR** (600 MHz, CD_2Cl_2): δ = −49.52 (CH_3^{11}), −46.09 (H^4), −15.10 (CH_3^{13}), −9.68 (H^5), 5.51 ($SiCH_3^{9}$), 7.80 (H^7), 10.24 (H^6), 38.00 (CH_3^{8}), 39.37 (CH_3^{12}), 50.43 (H^3), 58.00 (CH_3^{10}). **^{13}C-NMR** (150 MHz, CD_2Cl_2): δ = −64.55, −50.11,

12.96, 21.44, 33.36, 43.77, 59.41, 78.55, 87.34, 92.45, 141.13, 161.31. **EI-MS** (m/z [rel. int.]): 470.12 (100%), 506.09 (32%), 455.09 (26%). **Elemental Analysis**: calc. (found) for $C_{26}H_{30}Cl_2CrNSi$: C: 61.53 (61.11); H: 5.96 (5.91); N: 2.76 (2.70).

Complex 12

A solution of **6** (300 mg, 1.01 mmol, 1.00 eq) in THF (10 ml) was cooled to −90 °C before a 1.6 M solution of *n*-BuLi (631 µl, 1.01 mmol, 1.00 eq) was added dropwise over 15 min. The reaction mixture turned deep purple rapidly and was stirred for another 15 min at −90 °C. After warming up to rt this solution was added via cannula to a suspension of $CrCl_3(THF)_3$ (378 mg, 1.01 mmol, 1.00 eq) in THF (15 ml) and was stirred for 16 h to form a dark solution with a precipitate. The pulverulent precipitate was separated from the solution with a centrifuge and was washed with THF (3x2 ml) and pentane (2×10 ml) and dried under vacuum to yield the target complex **12** (131 mg, 312 µmol, 31%) as a green solid. **^{1}H-NMR** (600 MHz, CD_2Cl_2): δ = −51.70 (H^{11ax}), −49.44 (H^{11eq}), −48.94 (H^4), −23.73 (H^{10}), −12.66 (H^5), 1.07 (H^{13eq}), 2.54 (H^{13ax}), 3.25 (H^{12eq}), 3.63 (H^{12ax}), 6.84 (H^7), 11.23 (H^6), 34.87 (H^{14eq}), 35.99 (H^{15}), 49.85 (H^3). **^{13}C-NMR** (150 MHz, CD_2Cl_2): δ = −12.77, −6.48, 29.80, 64.35, 172.17. **EI-MS** (m/z [rel. int.]): 296.14 (100%), 346.07 (21%), 382.05 (20%), 418.02 (20%). **Elemental Analysis**: calc. (found) for $C_{22}H_{18}Cl_2CrN$: C: 63.02 (62.93); H: 4.33 (4.29); N: 3.34 (3.06).

Complex 13

A solution of **7** (300 mg, 963 µmol, 1.00 eq) in THF (8 ml) was cooled to −90 °C before a 1.6 M solution of *n*-BuLi (602 µl, 963 µmol, 1.00 eq) was added dropwise over 15 min. The resulting deep blue mixture was stirred for another 15 min at −90 °C. After warming up to rt this solution was added via cannula to a suspension of $CrCl_3(THF)_3$ (361 mg, 963 mmol, 1.00 eq) in THF (10 ml) and was stirred for 16 h to form a dark green solution. The solvent was removed under reduced pressure and after toluene (20 ml) was added the resulting suspension was stirred for 2 h. The toluene was removed under vacuum and the residue was extracted with a mixture of dichloromethane and pentane (1:1; 6 ml). This solution was dried under vacuum and the residue was crystallized by diffusion of pentane into a solution of dichloromethane. After the solid was washed with pentane (2×10 ml) complex **13** (112 mg, 259 µmol, 27%) was obtained as dark green crystals. **^{1}H-NMR** (600 MHz, CD_2Cl_2): δ = −53.32 (H^{11ax}), −51.26 (H^{11eq}), −48.63 (H^4), −25.93 (H^{10}), −11.88 (H^5), 1.01 (H^{13eq}), 2.59 (H^{13ax}), 3.30 (H^{12eq}), 3.80 (H^{12ax}), 6.88 (H^7), 10.99 (H^6), 35.91 ($H^{14ax/eq}$), 37.24 (H^{15}), 50.44 (H^3), 57.20 ($C\underline{H}_3{}^8$). **EI-MS** (m/z [rel. int.]): 310.16 (100%), 396.06 (84%), 360.08 (82%), 432.04 (34%). **Elemental Analysis**: calc. (found) for $C_{23}H_{20}Cl_2CrN$: C: 63.75 (63.73); H: 4.65 (4.45); N: 3.23(2.74).

Complex 14

A solution of **8** (300 mg, 782 µmol, 1.00 eq) in THF (6 ml) was cooled to −90 °C before a 1.6 M solution of *n*-BuLi (488 µl, 782 µmol, 1.00 eq) was added dropwise over 15 min. The reaction mixture turned deep blue rapidly and was stirred for another 15 min at −90 °C. After warming up to rt this solution was added via cannula to a suspension of $CrCl_3(THF)_3$ (293 mg, 782 mmol, 1.00 eq) in THF (15 ml) and was stirred for 14 h to form a dark solution with a precipitate. The pulverulent precipitate was separated from the solution with a centrifuge and was washed with THF (2 ml) and pentane (2×10 ml) and dried under vacuum to yield the target complex **14** (143 mg, 283 µmol, 36%) as a dark green solid. **^{1}H-NMR** (600 MHz, CD_2Cl_2): δ = −65.68 (H^{11ax}), −64.86 (H^{11eq}), −46.73 (H^4), −33.11 (H^{10}), −10.63 (H^5), 0.84 (H^{13eq}), 2.72 (H^{13ax}), 2.88 (H^{12eq}), 3.77 (H^{12ax}), 6.70 ($SiC\underline{H}_3{}^9$), 7.46 (H^7), 10.71 (H^6), 42.13 ($C\underline{H}_3{}^8$, H^{15}, $H^{14eq/ax}$), 50.40 (H^3). **^{13}C-NMR** (150 MHz, CD_2Cl_2): δ = −26.56, −17.04, 35.44, 69.54, 105.60, 166.90. **EI-MS** (m/z [rel. int.]): 468.10 (100%), 504.08 (68%), 432.13 (60%), 366.17 (54%), 489.06 (40%). **Elemental Analysis**: calc. (found) for $C_{26}H_{28}Cl_2CrNSi$: C: 61.78 (59.43); H: 5.58 (5.46); N: 2.77 (2.64).

Deposition Numbers 2048130 (for **10**), 2048131 (for **11**·1.3 CH_2Cl_2), 2048132 (for **13**·CH_2Cl_2), and 2048133 (for **14**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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